PATENT SPECIFICATION

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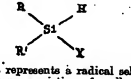
COMPLETE SPECIFICATION

Improvement in Organo-Silicon Halides

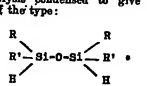
We, THE DOW CHEMICAL COMPANY, a company organised under the laws of the State of Michigan, United States of America, of Midland, State of Michigan, United States of America, (Assignees of ARTHUR JOHN BARRY, a citizen of the United States of America, of 3718, Ashman Street, Midland Michigan, United States of America), do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention concerns certain new organohalosilanes. These new compounds are diorgano-monohalosilanes having the general formula:

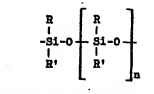


in which R represents a radical selected from the group consisting of aralkyl and aromatic radicals, R¹ represents a radical selected from the class consisting of alkyl, aralkyl and aromatic radicals, and X represents a halogen atom.

These compounds contain two different readily removable groups, namely a halogen atom and a hydrogen atom, both attached directly to the silicon atom in the molecule. The halogen atom may be displaced by reacting the compound with an alcohol, whereby the corresponding mono-alkoxy-diorgano-silane is produced. The diorgano-monohalosilanes may also be reacted with water, and the products of hydrolysis condensed to give compounds of the type:



Subsequently, the end-blocking hydrogen may be displaced by oxygen under mildly oxidizing conditions with the formation of further oxygen linkages between silicon atoms. In this way there may be built up polymers of high molecular weight containing in the molecule the radical:



in which n is a whole number.

It can thus be seen that diorgano-monohalosilanes are useful for the preparation of a wide variety of organo-siloxane polymers. They may also be used for treating normally hydrophilic materials such as fabrics, etc., to render such materials repellent to moisture.

The present invention consists in reacting an inorganic trihalosilane or, a mono-organo-dihalosilane containing one of the desired R or R¹ substituents, with at least its molecular equivalent of an organo-magnesium halide containing one of the desired R or R¹ substituents, in the presence of an ether as a reaction medium. The reaction is usually carried out at a low temperature, e.g. 0° C. or below. Together with the desired diorgano-monohalosilane, there are usually also produced other organo-halosilanes of varying degrees of organic substitution, e.g. a mono-organo-dihalosilane, a tri-organo-silane, etc. In general, the best yields of di-organo-monohalosilane are obtained when the starting materials comprise from 1.0 to 2.2 molecular equivalents of the organo-magnesium halide for each mol of trihalo-silane employed.

Trichlorosilane is preferably employed

as the trihalosilane, but trifluorosilane or tribromosilane may also be used. Any of the ethers ordinarily employed in carrying out Grignard reactions, e.g. dimethyl ether, diethyl ether or dibutyl ether, may be used as the medium for the reaction.

In practice, the Grignard reagent is usually added in a dropwise manner to the trihalosilane while maintaining the reaction mixture at a temperature of 0° C. or below with stirring. When the addition is complete, the product is allowed to stand for several hours, with stirring, during which period the temperature of the mixture approaches that of the room. The magnesium halide which forms may be separated from the reaction mixture by filtration, decantation, distillation, etc., after which the solution of organosilicon halides may be fractionally distilled to recover the diorgano-monohalosilane.

Diorgano-monohalosilanes containing two different hydrocarbon radicals may be prepared in a manner similar to that described above by employing a Grignard reagent prepared from a mixture of halohydrocarbons containing the desired organic radicals. An organo-magnesium halide may also be reacted with a monoorgano-dihalosilane to produce a diorgano-monohalosilane.

The following examples describe a number of ways in which the principle of the invention has been applied but are not to be construed as limiting its scope:

EXAMPLE 1.

A solution of 478 grams (3.53 mols) of trichlorosilane and approximately 1759 grams of benzene was cooled in a bath of ice and salt, and 3132 grams of an ethereal solution containing approximately 1459 grams (7.42 mols) of *p*-methylphenyl magnesium bromide was added with stirring during a period of about 2.25 hours. After adding the *p*-methylphenyl magnesium bromide, the mixture was permitted to stand, with stirring, for several hours, and subsequently the magnesium bromide was removed by filtration. The filtrate was then fractionally distilled, first to remove the solvents and thereafter to separate the di-*p*-methylphenyl monochlorosilane. As a fraction boiling at temperatures between 112° and 117° C. at from 0.45 to 0.55 mm. pressure, there was obtained 358 grams (1.43 mols) of di-*p*-methylphenyl monochlorosilane. The product is a clear colorless liquid having a specific gravity of d_4^{20} =1.096, and an index of refraction of n_D^{20} =1.5701.

EXAMPLE 2.

By procedure similar to that described in Example 1, phenyl magnesium chloride may be reacted with trichlorosilane in the presence of diethyl ether as a reaction medium to produce diphenyl monochlorosilane, $(C_6H_5)_2HSiCl$, a colorless liquid, boiling at 143° C. at 10 mm. pressure; d_4^{20} =1.118; n_D^{20} =1.581.

EXAMPLE 3.

By procedure similar to that described in Example 1, benzyl magnesium bromide was reacted with trichlorosilane in the presence of diethyl ether as a reaction medium. As a fraction boiling at temperatures between 102° and 110° C. at 0.4 mm. pressure, dibenzyl monochlorosilane was obtained. The product was a colorless liquid having an index of refraction of n_D^{20} =1.5721

EXAMPLE 4.

An ethereal solution containing 4.0 gram mols of phenyl magnesium bromide was added slowly and with stirring to a solution containing 10.0 gram mols of mono-ethyl dichlorosilane in benzene, while maintaining the reaction mixture at a temperature of −50° C. or lower, by immersion in a bath of acetone and solid carbon dioxide. When the addition was complete, the mixture was allowed to stand overnight with stirring. The product was filtered to remove the magnesium salts, and subsequently was fractionally distilled. Ethyl phenyl monochlorosilane, $(C_6H_5)(C_2H_5)SiClH$, was obtained as the fraction distilling at 111° C. at 50 mm. absolute pressure. The compound is a colorless liquid, n_D^{20} =1.5103.

EXAMPLE 5.

By procedure similar to that described in Example 4, methyl phenyl monochlorosilane may be prepared from monomethyl dichlorosilane and phenyl magnesium bromide. $(CH_3)(C_6H_5)SiHCl$ is a colorless liquid, distilling at 113° C. at 100 mm. absolute pressure; d_4^{20} =1.043; n_D^{20} =1.5157.

EXAMPLE 6.

Operating in a manner similar to that described in Example 4, isopropyl dichlorosilane may be reacted with *p*-chloro-

phenyl magnesium bromide to produce *p*-chlorophenyl isopropyl monochlorosilane. The compound is a colorless liquid, distilling at from 134° to 134.75° C. at 30 mm. absolute pressure; $d_4^{20}=1.115$; $n_D^{20}=1.5239$.

EXAMPLE 7.

By procedure similar to that described in Example 4, monoethyl dichlorosilane and benzyl magnesium chloride may be reacted to produce benzyl ethyl monochlorosilane, distilling at 114—116.5° C. at 30 mm. absolute pressure; $d_4^{20}=1.019$; $n_D^{20}=1.5130$.

Operating in a manner similar to that described in the preceding examples, monomethyl dibromosilane and benzyl magnesium chloride may be reacted to produce benzyl methyl monobromosilane; phenyl magnesium bromide may be reacted with tribromosilane to produce diphenyl monobromosilane; dinaphthyl monochlorosilane may be obtained from the reaction of naphthyl magnesium chloride with naphthyl dichlorosilane; *p*-bromophenyl magnesium chloride may be reacted with isopropyl dichlorosilane to produce *p*-bromophenyl isopropyl monochlorosilane; phenyldodecyl monochlorosilane may be obtained from the reaction of phenyl magnesium bromide with dodecyl dichlorosilane; phenyl magnesium bromide may be reacted with octadecyl dichlorosilane to produce phenyl octadecyl monochlorosilane.

Having now particularly described and ascertained the nature of our said invention, and in what manner the same is to be performed, we declare that what we claim is:—

1. A process of making organo-halosilanes having the general formula:

wherein R is an aralkyl or aromatic radical, R¹ is an alkyl, aralkyl or an aromatic radical, and X is a halogen, which comprises reacting an inorganic trihalosilane, or a mono-organo-dihalosilane containing one of the desired R or R¹ substituents, with at least its molecular equivalent of an organo-magnesium halide containing one of the desired R or R¹ substituents, in the presence of an ether as a reaction medium.

2. A process in accordance with claim 1, wherein the reaction is carried out at temperatures of 0° C. and below.

3. A process in accordance with claim 1 or 2 wherein an inorganic trihalosilane is reacted with approximately two molecular equivalent weights of an organo-magnesium halide.

4. A process in accordance with any one of the preceding claims wherein trichlorosilane is reacted with approximately two molecular equivalent weights of an organo-magnesium halide.

5. A process in accordance with claim 1 or 2, wherein a mono-organo-dihalosilane is reacted with approximately one molecular equivalent weight of an organo-magnesium halide.

6. A process in accordance with claim 1 or 2, wherein a monoalkyldichlorosilane is reacted with approximately one molecular equivalent weight of an organo-magnesium halide.

7. A process in accordance with any one of the preceding claims, wherein the organo-magnesium halide is an aryl-magnesium chloride or bromide.

8. A process of making an organo-halosilane having the general formula:

wherein R is an aralkyl or aromatic radical, R¹ is an alkyl, aralkyl, or an aromatic radical and X is a halogen, as described in any one of the Examples 1 to 7 inclusive, or with any of the alternatives hereinbefore mentioned.

9. An organo-halosilane having the general formula:

wherein R is an aralkyl or aromatic radical, R¹ is an alkyl, aralkyl or an aromatic radical and X is a halogen, when prepared by the method of any of the Claims 1 to 8, inclusive.

Dated the 27th day of January, 1947.

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